Name _____ AP Chemistry

Reaction Mechanisms

Once the rate law has been determined experimentally, several mechanisms, or paths, can be proposed. The correct mechanism has to match the data from the experiment, i.e. the experimentally-determined rate law. A reaction mechanism is a series of steps to explain how a reaction happens. The steps must add up to give the overall reaction. Furthermore, these steps will occur at different rates. The slowest step will be what controls the rate so it is called the rate determining step. The rate law will be based on the rate determining step.

Based on the number of species colliding, the molecularity can be described. For one item, the reaction is unimolecular and if there are two species, it is considered bimolecular, etc. A unimolecular reaction or step of a reaction is always first order while a bimolecular one is second order. The rate law can be predicted based on the molecularity of the reaction or step of a reaction.

Example #1:

The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is

$$2\ NO_2\ (g) + F_2\ (g) \rightarrow 2\ NO_2F\ (g)$$

The experimentally determined rate law is: rate = k $[NO_2][F_2]$. Is the suggested mechanism below acceptable for this reaction?

$$NO_2 + F_2 \rightarrow NO_2 + F \text{ (slow)}$$

$$F + NO_2 \rightarrow NO_2F \text{ (fast)}$$

As part of the reaction mechanisms, there are two special species that can appear. Define the two below:

- Catalyst
- Intermediate

Example #2

The decomposition of hydrogen peroxide is catalyzed by iodide ion. The catalyzed reaction is thought to proceed by a two-step mechanism:

$$H_2O_2\ (aq) + I^-\ (aq) \rightarrow H_2O\ (l) + IO^-\ (aq)\ (slow)$$

$$IO^-\ (aq) + H_2O_2\ (aq) \rightarrow H_2O\ (l) + O_2\ (g) + I^-\ (aq)\ (fast)$$

(a) Write the chemical reaction for the overall reaction.
(b) Identify any intermediates and any catalysts.

Problems

1) Predict the rate law for each of the following reactions:
   (a) $NO_3 + O_3 \rightarrow NO_2 + O_2$
   (b) $I_2 \rightarrow 2\ I$
   (c) $NO + O_2 \rightarrow NO_3$
2) For the reaction $2\ H_2\ (g) + 2\ NO\ (g) \rightarrow N_2\ (g) + 2\ H_2O\ (g)$, the experimental rate law is rate = $k\ [H_2][NO]^2$. The following proposed mechanism is given:

$$2\ NO \leftrightarrow N_2O_2\ (fast)$$

$$N_2O_2 + H_2 \rightarrow H_2O + N_2O\ (slow)$$

$$N_2O + H_2 \rightarrow N_2 + H_2O\ (fast)$$

   (a) Identify the intermediates.
   (b) Is this mechanism appropriate for the rate law?
3) The following mechanism has been proposed for the gas-phase reaction with H_2 with ICl:

$$H_2\ (g) + ICl\ (g) \rightarrow HI\ (g) + HCl\ (g)$$

$$HI\ (g) + ICl\ (g) \rightarrow I_2\ (g) + HCl\ (g)$$

   (a) Write the balanced equation for the overall reaction.
   (b) Identify any intermediates in the mechanism.
   (c) Write rate laws for each elementary reaction (i.e. each step) in the mechanism.
   (d) If the first step is slow and the second one is fast, what rate law do you expect to be observed for the overall reaction?